

# **JP2000-345026 (C rporation Kurar )**

## **Title**

Heat Gelable PU Emulsion

## **Objective**

To develop artificial leather having excellent touch with a heat gelable PU emulsion having long term storage stability.

## **Abstract**

To achieve above objective the use of two nonionic surfactants, 5-15pph of non ionic surfactant A having 13-17 of HLB and 1-20 pph of non ionic surfactant B having 8-15 of HBL shown below, are used in preparation of PU water dispersion.

R-O- (CH<sub>2</sub>-CH<sub>2</sub>-O-) <sub>x</sub>- H

## **Back ground of invention**

In production of artificial leather using Polyurethane resin, there are two technologies. In the first approach, fabrics are impregnated in polyurethane resin dissolved in an organic solvent, mainly DMF. Then the fabrics are immersed into water, and DMF is removed. (Wet method) In the second approach, fabrics are impregnated in polyurethane resin dissolved in an organic solvent or water dispersions, and the fabrics are dried. (Dry method). Wet method provides natural leather like excellent touch but use of organic solvent is indispensable. In dry method using water dispersion, touch is inferior to the artificial leather made with wet process in spite of eliminating undesirable organic solvent in the production process. However these days, artificial leather industry is expected to move from wet process to dry process due to the environmental consideration. Water dispersion impregnated in the fabric is designed to gel very quickly when heated up. This will prevent the migration of PU resin during drying process of fabric containing PU dispersion. Some nonionic surfactant promotes gelation of water dispersion as described in JP2-308844. However the technology suggested in above patent do not offer good performance, where long pre-drying process is indispensable to eliminate migration of resin at drying process.

## **Principle**

Non-ionic surfactant (A) having HLB of 13-17 offer stable emulsion and non-ionic surfactant (B) having HLB of 8-15 promote gelation of PU resin. 5-15 pph of surfactant A and 100 pph of NCO terminated pre-polymer made with polyol, isocyanate and chain extender are emulsified. After completion of chain extension reaction, 1-20pph of surfactant B and 100 pph of emulsion prepared above are mixed together. Thus, heat gelable PU dispersion is obtained.

## **Experimental session**

### **Test method**

**G 1 Time:** 25g of PU dispersion were charged to a test tube of 20mm diameter. The test tube is put in an oven of 90 deg C. Every one minute, the sample was

checked if the PU dispersion still have flow capability. The time when the PU dispersion loses flow capability is counted as gel time.

**Storage stability:**

After preparation of PU dispersion, the sample is stored at 25 deg C for 24 hrs. If the sample still have flow capability to soak the fabric, storage stability is judged to be acceptable, otherwise stability is judged to be unacceptable.

**Modulus at 90 deg C**

100-micron film prepared with the PU dispersion by drying at 50 deg C are subjected to a instrument, named FR REOSPECTLAR DVE-V4. The modulus is measured at 11Hz and 90 deg C.

**Touch/Feeling**

If the sheets made with the PU dispersion and non-woven fabric has natural leather like feeling, the quality is judged as acceptable. Otherwise judged to be unacceptable.

**Migration of PU resin during drying process**

Cross section of the sheet prepared with PU dispersion and non-woven fabric was inspected with a SEM if migration of PU resin occurs during drying process.

**Raw material used for preparation of PU dispersion**

**Table -1**

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PMSA1850: 1850 MW polyester diol made with 3-methyl-1,5 pentane diol and adipic

acid/Sebacic acid (1/3)

PHC 2000: Poly hexa methylene carbonate of 2000mw

PTG 1000: Poly tetra-methylene glycol of 1000 mw

PBA 1000: Poly butylene adipate of 1000mw

TDI: 2,4-Toluene di-isocyanate

MDI: 4,4' di-phenyl methane di-isocyanate

DMPA: 2,2 bis (hydroxy methyl) propionic acid

MEK: Methyl ethyl ketone

TEA: Tri-ethyl amine

DETA: Di ethylene tri-amine

IPDA: Isophorone diamine

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**Preparation of non woven fabric**

**Reference 1**

A mixture of high flow poly ethylene/ Nylon (40pph/60pph) is subjected to a spinning and drawing process. The fiber obtained, 4 denier x 51mm long are fabricated into a non-woven fabric of 0.16g/cm<sup>3</sup> density. The fabric was heated and polyethylene is melted as binder and 0.285g/cm<sup>3</sup> of non- woven fabric having flat surface was prepared. The fabric made in this procedure is named **Fabric -1**.

### **Ref r nc 2**

A mixture of 70pph of polyethylene terephthalate and 30pph of low-density polyethylene is subjected to spinning and drawing process. Fibers of 4 denier x 51mm long are fabricated into non-woven fabric with a same procedure in Reference 1. The fabric is exposed into the hot water and let shrinks by 30% for the area. With this treatment the polyethylene is melted, and helps bind the fiber together. Thus flat surface non-woven fabric of 0.35g/cm<sup>3</sup> was prepared. This fabric was named, **Fabric -2**

### **Reference 3**

Polyethylene terephthalate fibers, was shrunk by 25% in the 70 deg C of hot water and the fiber, 2 denier x 51mm, are fabricated into a web of 240g/m<sup>2</sup> of surface density. The web was soaked into a hot water of 70 deg C for 2min so that the fabric shrinks by 56% against original area. The web was pressed at 155 deg C and a fabric of 360g/m<sup>2</sup> surface density and 1.2mm thickness, and 0.30g/cm<sup>3</sup> density was obtained. The fabric was soaked into 5 % solution of silicone based water proof agent and was dried at 130 deg C for 30min. The non-woven fabric made with this procedure was named **Fabric-3**

### **Example 1**

#### **Preparation of PU emulsion**

600g of PMSA 1850, 114.0g of TDI and 7.9 g of DMPA are charged to a three neck round bottle flask and was heated for 2hrs at 90 deg C under nitrogen atmosphere.

227.5g of toluene was added to above NCO terminated pre-polymer and was agitated. Then, the temperature was cooled to 40 deg C, and 6.0g of TEA was added and agitated again for additional 10min.

An emulsifier consisting of 53.2 g of non ionic surfactant, EMALUGEN 147 from Kao Soap/ HLB =16.3 (polyoxy ethylene rauryl ether), and 680g of distilled water was mixed with above pre-polymer, and was agitated with a homo mixer for one min. Immediately after agitation, a solution containing 13.2 g of DETA, 10.9 g of IPDA and 230g of distilled water was added to above emulsion, and the mixture was again agitated with a homo-mixer for 1min, and chain extension reaction was completed.

Toluene was eliminated by evaporation and after adding distilled water, and polyurethane emulsion containing 40% solid was obtained.

80 pph of the emulsion prepared in above procedure, a solution consisting of 20 pph of distilled water and 8pph of a gelation promoting agent made with water, poly oxy ethylene rauryl ether type non ionic surfactant (EMALUGEN109,HLB=13.) and calcium chloride( 5:4:1) were mixed together and **PU emulsion-1** was obtained. Gel time of this dispersion was 4min.

#### **Preparation of artificial leather**

**Fabric -1** was soaked to the **PU emulsion-1**. After wring the emulsion out with a pressed roller the fabric was subjected to a hot bath of 90 deg C for I min, and was dried in a dry oven of 130 deg C for 30min. The artificial leather sheet made was subjected to hot toluene, and the sheet was squeezed with a press role of 2kg/cm<sup>2</sup> five times and polyethylene was removed. Resin weight in the sheet was

53%. The sheet showed natural leather like feeling and touch, and it was confirmed that there was no resin migration.

### **Comparative test 1**

PU dispersion was prepared according to a procedure described in Example 1 except for one change, where non-ionic surfactant was changed from EMALUGEN 147 to EMALUGEN 130 having HLB of 18.1. The emulsion prepared with this procedure was named **PU emulsion-2**.

Gel time of this emulsion was 20min.

The emulsion has flow capability after 24 Hrs.

Modulus of the film made according the test method was  $3 \times 10^7$  dyn/cm<sup>2</sup>

Artificial leather was prepared with **PU emulsion 2** according to the procedure described in Example-1. When the sheet was soaked to a hot water, the PU emulsion breaed from the sheet. The sheet prepare in tha above process was subjected to hot toluene and polyethylene was removed. The resin content in the sheet was 48%, and migration of PU resin in the sheet was observed. Feeling or touch of the sheet was paper like and was not acceptable.

### **Example 2**

250g of PHC 2000, 250g of PTG 1000 and 105.8g of TDI and 6.38g of DMPA were charged to a three neck flak. The mixture was heated at 90 deg C for 2 hrs, and NCO terminated pre-polymer was prepared.

191.7g MEK was added to above pre-polymer, and the mixture was agitated, then the temperature was cooled to 40 deg C. 4.81g of TEA was added to this pre-polymer , and was agitated for 10 min.

A solution consisting of 44.8g of non-ionic surfactant, EMULGEN 147(HLB=16.3), and 910.4g of distilled water was blended to above pre-polymer. This mixture was agitated with a homo-mixer for 1 min. Immediately after agitation for 1 min, a solution consisting of 9.5g of DETA and 7.84g of IPDA and 240g of distilled water was added. The mixture was agitated for another one min, and chain reaction was completed.

MEK in above emulsion was removed by evaporation, and distilled water was added again so that solid content of the emulsion comes to 40%.

80pph of above emulsion and 8 pph of gel promoting agent consisting of water, poly oxy ethylene rauryl ether type nonionic surfactant, EMULGEN 106(HLB=10) and calcium chloride in a blending ratio (5:4:1) was mixed together. Thus, the PU emulsion prepared was named **PU Emulsion-3**

Gel time of this emulsion was 6 min.

This emulsion was fluid after 24 hrs.

A film made with emulsion showed modulus of  $4.3 \times 10^7$  dyn/cm<sup>2</sup> at 90 deg C.

Non woven fabric-2 was soaked into this emulsion. After squeezing with a press role five times, the sheet was subjected to a steam of 0.2kgf/cm<sup>2</sup>. Then, the sheet was heated at 130 deg C for 30 min. Thus, a sheet was tha

The sheet was treated with hot toluene, and was squeezed with a press role and polyethylene was removed. Solid content of the sheet was 40%. The sheet showed natural leather like feeling and touch.

#### **Comparative test-2**

Heat gelable PU emulsion was prepared according to a procedure written in Example 2 except for one change, where 4 pph of gel promoting agent consisting of water, poly oxy ethylene rauryl ether type nonionic surfactant, EMULGEN 120(HLB=15.3), and calcium chloride in a mixing ratio of 5:4:1 was used. The Emulsion prepared in this procedure was named **PU Emulsion-4**.

Gel time of this emulsion was 20 min.

This emulsion showed flow capability after 24 hrs.

The film made with this emulsion showed  $4.2 \times 10^7$  dyn/cm<sup>2</sup> at 90 deg C.

An artificial leather sheet was made with this emulsion-4 and a procedure written in Example 1 after extraction of polyethylene fiber with toluene. Resin content of the sheet was 40%. However migration of PU resin was observed in the sheet, touch of the sheet was coarse, not soft enough like natural leather.

#### **Comparative test-3**

An PU emulsion was prepared according to the procedure written in Example one except for one change, where 15.3 g of polyoxy ethylene rauryl ether type nonionic surfactant, EMULGEN 120(HLB=15.3)was used as emulsifier. The emulsion prepared here was named **Emulsion-5**

Gel time of this PU emulsion was 3 min.

This emulsion lost flow capability, and gelled after 24 hrs.

Sheet could not be made with this dispersion.

PU film made with dispersion showed modulus of  $2.9 \times 10^7$  dyn/cm<sup>2</sup> at 90 deg C.

#### **Comparative test- 4**

A PU emulsion was prepared according to a test method written in Example 2 except for one change, where 137.8g of nonionic surfactant, EMULGEN 147(HLB=16.3), was used. The PU emulsion made with this procedure was named **Emulsion-6**.

Gel time of this emulsion was 30min.

This emulsion was fluid after 24 hrs.

The film made with emulsion showed modulus of  $4.2 \times 10^7$  dyn/cm<sup>2</sup>.at 90 deg C

An artificial leather sheet made with **emulsion-6** and a procedure written in Example 2 was soaked to hot water. However minor breading of emulsion was observed. Resin content of the sheet was 39%. The touch of the sheet was soft enough but tends to show wrinkle. Migration of resin in the sheet was observed by SEM analysis.

#### **Example 3**

500g of PBAI, 142.3g of TDI and 6.93g of DMP were charged to a three-neck flask under nitrogen atmosphere, and was heated at 90 deg C for 2 hrs. Then, NCO terminated pre-polymer was prepared, and 206.2g of toluene was added to above pre-polymer.

After agitation of above pre-polymer, the temperature was cooled to 40 deg C, and 5.23g TEA was added. After agitation for 10min, a mixture of 35.7g of poly oxy ethylene oleyl ether type nonionic surfactant, EMULGEN 430 (HLB= 16.2) and 602g of water was added, and the mixture was agitated for 1 min.

Immediately after agitation, a mixture of 13.4 g of DETA , 11.1 g of IPDA and 207g.5g of water was added, and agitated further for another 1 min, then chain extension reaction was completed.

Toluene in the emulsion was removed by distillation, and distilled water was added so that solid content comes to 40%.

80 pph above emulsion and 5 pph gel promoting agent consisting of water, poly oxy ethylene oleyl ether type nonionic surfactant, EMULGEN 409P(HLB=12.0) and calcium chloride in 5:4:1 ratio was mixed together. The PU emulsion, thus produced was named **Emulsion-7**.

Gel time of this emulsion was 7 min.

This emulsion was fluid after 24 hrs.

A film made with this emulsion showed  $2.5 \times 10^7$  dyn/cm<sup>2</sup> at 90 deg C.

Non **woven fabric -3** were soaked to the emulsion-7 and were wring out. The woven fabric was subjected to a steam of 0.5kg/cm<sup>2</sup> for 1 min, and was dried at 130 deg C for 30 min. The resign content of the artificial leather produced was 43%. Migration of the resign was not observed, and the artificial leather showed natural leather like soft touch.

#### **Comparative test 5**

PU emulsion was prepared according to a procedure described in example 3 except for one change, where 35.7g of nonionic surfactant, EMULGEN 420(HLB=12.0) was used.

The PU emulsion prepared was named **PU Emulsion-8**.

Gel time of this emulsion was 2 min.

This emulsion gelled after 24 hrs.

Sheet could not be prepared with this emulsion.

The film made with this emulsion by drying showed modulus of  $2.5 \times 10^7$  dyn/cm<sup>2</sup> at 90 deg C.

#### **Comparative test 6**

PU emulsion was prepared according to a procedure described in Example 3 except for one change, where 8 pph of gel promoting agent consisting of water, nonionic surfactant, EMULGEN 109P ( HLB=13.6) and calcium chloride in a ratio of 5:4:1 was used.

This PU emulsion was named **PU Emulsion-9**.

Gel time of this emulsion was 1 min.

This emulsion gelled after 24 hrs

Sheet could not be made with this emulsion.

A film made with this emulsion after drying showed modulus of  $3.1 \times 10^7$  dyn/cm<sup>2</sup> at 90 deg C

## **Summary**

As shown in table-2, Example 1, 2 and 3 provided pertinent gel time, heat gelable characteristics, and storage stability. Artificial leather prepared with emulsions made in Example 1 2 and 3 did not show any resign migration and provided natural leather like soft touch.

On the other hand, the emulsion consisting of high HLB non-ionic surfactant-I as shown in comparison test-1 and the emulsion containing high level of surfactant-II as shown in comparative test-2 did not give sufficient gelation. The artificial leather obtained with those emulsions showed migration of the resign, and touch of the leather was not as soft as natural leather.

The emulsions consisting of low HLB non-ionic surfactant-I as shown in comparative test-5 and the emulsions containing low level of non-ionic surfactant-II as shown in comparative test-6 gave too short gel time to prepare artificial leather.

**Table 2**

			Emulsion	non-woven fabric	modulus	gel time	storage	stability	migration	touch
Example 1	1	1	Dyn/cm <sup>2</sup>	(min)	(24 h)					
			3 x 10 <sup>7</sup>	4	OK	OK	OK			
Example 2	3	2	4.3 x 10 <sup>7</sup>	6	OK	OK	OK			
Example 3	7	3	2.5 x 10 <sup>7</sup>	7	OK	OK	OK			
Compa 1	2	1	3.0 x 10 <sup>7</sup>	20	OK	NO	NO			
Compa 2	4	2	4.2 x 10 <sup>7</sup>	20	OK	NO	NO			
Compa 3	5	-	3.0 x 10 <sup>7</sup>	3	NO	-	-			
Compa 4	6	2	4.2 x 10 <sup>7</sup>	15	OK	NO	NO			
Compa 5	8	-	2.5 x 10 <sup>7</sup>	2	NO	-	-			
Compa 6	9	-	3.1 x 10 <sup>7</sup>	1	NO	-	-			

## **Claim**

I) This invention claims heat gelable polyurethane emulsion made with 100 pph polyurethane, 5-15 pph of nonionic surfactant (I) having HLB of 13.0-17.0 shown in chemical formula (I), 1-20 pph of nonionic surfactant (II) having HLB of 8-15.0 shown in chemical formula(I), which is lower HLB than surfactant (I) and water.



II) In the general chemical formula in claimed 1, this invention claims heat gelable emulsion, where R is rauryl group

III) Heat gelable emulsion in claim 1 and 2, this invention claim the use of 5-50 pph of inorganic salt together against 100 pph of nonionic surfactant (II).

IV) In a production of heat gelable polyurethane emulsion with polyol, di-isocyanate and chain extender this invention claims a process described below.

1) Pre-polymer is prepared with polyol, di-isocyanate and chain extender if necessary.

2) Polyurethane pre-polymer is emulsified with 5-15pph of nonionic surfactant (1) having HLB of 13-17 shown below against 100pph of pre-polymer.

R-O-(CH<sub>2</sub>-CH<sub>2</sub>-O-)<sub>x</sub>-H-----(1)

3) After chain extension reaction of polyurethane pre-polymer is completed

4) The invention claims production process of heat gelable PU dispersion, where 1-20 pph of nonionic surfactant having HLB of 8.0-15.0 against 100pph pre-polymer is blended to the emulsion in claim 3) in IV .

V) This invention claims heat gelable polyurethane emulsion, where 100micron thick film made with this polyurethane emulsion claimed any of claim (I),(II) and (III) by drying up at 50 deg C provide modulus of  $2.0 \times 10^7$ - $5.0 \times 10^8$  dyn/cm<sup>2</sup>

VI) This invention claims production process of artificial leather, where heat gelable polyurethane emulsion claimed in any of (I),(II),(III), and (IV) are soaked with non woven fabric and are coagulated.

VII) This invention claims a production process of artificial leather claimed in (VI), where heat gelable polyurethane emulsion is coagulated in either hot water of 70 deg C or is coagulated under steam.